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SPECIFIC HEAT OF FLUIDS2. THE SPECIFIC HEAT AND THE TEMPERATURE RELATION
OF SPECIFIC HEATS OF ALIPHATIC HALOGEN DERIVATIVES

V. Ya. Kurbatov

The experiments [by V. Ya. Kurbatov and coworkers] were carried out by the 'combination method'. Wide test tubes held platinum or quartz flasks (depth 50-75 mm) of the test liquid. The tubes were placed in two different liquids, boiling at definite temperatures. A mixer and a thermometer, which had been calibrated for position and temperature, were located 25-60 mm deep in the test liquid. At transfer they were removed carefully so that the loss of liquid on the thermometer and the loss due to evaporation were both exceedingly small. Weighing was done after the experiment. Radiation losses during transfer were measured experimentally.

When crystal substances were placed in these flasks, they were packed together by thin platinum-wire spirals. Volatile substances were enclosed in quartz flasks; the necks of the flasks were then sealed partially so that a thermometer could just barely be inserted. The flasks were cooled in the test tubes by lowering the latter into acetone cooled by liquid-air drops. The temperature was held within limits of $\pm 0.2^\circ$.

Boden thermometers were always checked according to substances of a definite boiling point and according to their position in the flask.

Substances, supplied by Kahlbaum, Poulenc, etc., were carefully distilled and desiccated by a dry-air stream in thoroughly dry instruments. Depending on availability of the substances, we tried to obtain either a constant point or, in the case of substances expensive or hard to purify (for example, to free dimethyl benzene from its isomers), as indicated in the description of each experiment, a range of boiling points within 0.2° to 0.5° .

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The formulas were calculated from these experiments and contrasted with the experimental data of other observers.

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1. Bromomethane (Methyl Bromide)
 $\text{CH}_3\text{Br} = 94.9$; Boiling Point 4.70 degrees ± 0.05 degrees
 Experimental Data of V. Kurbatov
 (Experiments in a Sealed Flask)
2. Iodomethane (Methyl Iodide)
 $\text{CH}_3\text{I} = 141.9$; Boiling Point 42.70 degrees
3. Dichloromethane (Methylene Chloride)
 $\text{CH}_2\text{Cl}_2 = 84.94$; Boiling Point 41.58 degrees
4. Dibromomethane (Methylene Bromide)
 $\text{CH}_2\text{Br}_2 = 173.56$; Boiling Point 97.3 degrees
5. Diiodomethane (Methylene Iodide)
 $\text{CH}_2\text{I}_2 = 267.9$; Boiling Point 180.4 degrees
6. Trichloromethane (Chloroform)
 $\text{CHCl}_3 = 119.39$; Boiling Point 61.21 degrees
 Experimental Data of V. Kurbatov
 Comparison With Data of Other Observers
7. Tribromomethane (Bromoform)
 $\text{CHBr}_3 = 252.9$; Boiling Point 150.9 degrees
 The Experimental Data of V. Kurbatov
 Comparison of Experiment and V. Kurbatov's Formula Showing Very Good Agreement

COMPARISON WITH OTHER DATA

8. Tetrachloromethane (Carbon Tetrachloride)
 $\text{CCl}_4 = 153.84$; Boiling Point 76.78 degrees
 Experimental Data of V. Kurbatov
 Comparison With the Data of Other Observers
9. Tetrabromomethane (Carbon Tetrabromide)
 $\text{CBr}_4 = 331.68$; Boiling Point 192.2 degrees
 Experimental Data of V. Kurbatov
10. Chloroethane (Ethyl Chloride)
 $\text{C}_2\text{H}_5\text{Cl} = 64.50$; Boiling Point $+14.0$ degrees
 Experimental Data of V. Kurbatov
11. Bromoethane (Ethyl Bromide)
 $\text{C}_2\text{H}_5\text{Br} = 108.96$; Melting Point -119 ; Boiling Point $+38.4$ degrees
 Experimental Data of V. Kurbatov
12. Iodothane (Ethyl Iodide)
 $\text{C}_2\text{H}_5\text{I} = 155.96$; Boiling Point 72.1 degrees
 Experimental Data of V. Kurbatov

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13. 1,2-Dichloroethane (Ethylene Chloride)
 $C_2H_4Cl_2$ = 98.95; Boiling Point 83.7 degrees
 Experimental Data of V. Kurbatov
14. 1,1-Dichloroethane (Ethylidene Chloride)
 CH_3CHCl_2 = 98.95; Boiling Point 57.5 degrees
 Experimental Data of V. Kurbatov
15. 1,2-Dibromoethane (Ethylene Bromide)
 $C_2H_4Br_2$ = 187.87; Boiling Point 131.1 degrees
16. 1,2-Tetrachloroethane (Acetylene Tetrachloride)
 $[CHCl_2]_2$ = 167.8; Boiling Point 147.1 degrees
 Experimental Data of V. Kurbatov
 Data of Other Observers
17. 1,2-Tetrabromoethane (Acetylene Tetrabromide)
 $C_2H_2Br_4$ = 345.7; Boiling Point 250 degrees
18. 1,2-Dichloroethane (Dichloroethylene)
 $ClHC : CHCl$ = 97.02; Boiling Point 55.8 degrees
19. Trichloroethene (Trichloroethylene)
 $CHCl : CCl_2$ = 132.52; Boiling Point 88.2 degrees
20. 1,2-Tetrachloroethane (Perchloroethylene)
 $CCl_2 : CCl_2$ = 165.8; Boiling Point 121.2 degrees
21. 1,2-Pentachloroethane (Pentachloroethylene)
 $CHCl_2CCl_3$ = 203.31; Boiling Point 161.9 ± 0.2 degrees
22. 1-Chloropropane (Propyl Chloride)
 $CH_3CH_2CH_2Cl$ = 78.52; Boiling Point 46.5 degrees
23. 1-Bromopropane (Propyl Bromide)
 $CH_3CH_2CH_2Br$ = 122.98; Boiling Point 70.8 degrees
24. 1,2-Dichloropropane (Propylene Chloride)
 $CH_3CH_2CHCl_2$ = 149.6; Boiling Point 98.2 degrees
25. 1,2-Dibromopropane (Propylene Bromide)
 $CH_3CHBrCH_2Br$ = 201.9; Boiling Point 141.6 degrees
26. Trimethylene Bromide
 $CHBrCHCH_2Br$ = 201.9; Boiling Point 165.4 degrees
27. 1,2,3-Trichloropropane
 $ClCH_2CHClCH_2Cl$ = 147.2; Boiling Point 153.2 degrees ± 0.2 degrees
28. 1,2,3-Tribromopropane
 $BrCH_2CHBrCH_2Br$ = 280.80; Boiling Point 220.3 ± 0.2 degrees
 Experimental Data of V. Kurbatov
29. 1-Bromobutane (Butyl Bromide)
 $CH_3CH_2CH_2CH_2Br$ = 136.99; Boiling Point 100.2 degrees
30. 1-Chloro-2-dimethylethane (Isobutyl Chloride)
 $(CH_3)_2CHCH_2Cl$ = 92.53; Boiling Point 68.5 degrees

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31. 1-Bromo-2-dimethylethane (Isobutyl Bromide)
 $(\text{CH}_3)_2 \text{CHCH}_2\text{Br} = 136.99$; Boiling Point 92.2 degrees
32. 1-Chloro-3-dimethylpropane (Isocamyl Chloride)
 $(\text{CH}_3)_2 \text{CHCH}_2\text{CH}_2\text{Cl} = 106.55$; Boiling Point 99.09 degrees
33. 1-Bromo-3-dimethylpropane (Isocamyl Bromide)
 $(\text{CH}_3)_2 \text{CHCH}_2\text{CH}_2\text{Br} = 151.11$; Boiling Point 119.1 degrees
34. 1-Iodo-3-dimethylpropane (Isocamyl Iodide)
 $(\text{CH}_3)_2 \text{CHCH}_2\text{CH}_2\text{I} = 198.01$; Boiling Point 146.8 degrees

Table 1. Specific Heats of Aliphatic Halogen Derivatives

The compilation in Table 1 of the linear formulas for specific heat, as might have been expected, shows that the introduction of heavier halogens or the increase in number of halogens sharply reduces both constant and derivatives in the formula. For example: in the case of CCl_4 when we have 8 percent carbon, the ratio $(\text{CCl}_4/\text{CBr}_4)$ of specific heats is $\frac{0.194}{0.091} \approx 2.1$, while the ratio $(\text{CBr}_4/\text{CCl}_4)$ of molecular weights is $\frac{332}{153} \approx 2.1$, but ratio (Br/Cl) of the halogens themselves is $\frac{79.98}{35.5} \approx 2.2$. The same pattern applies for $\text{C}_2\text{H}_2\text{Cl}_4$ and $\text{C}_2\text{H}_2\text{Br}_4$. The ratio of specific heats is $\frac{0.209}{0.103} \approx 2.0$. The ratio of molecular weights is $\frac{346}{168} \approx 2.0$. This confirms the law to the effect that the specific heat of liquids is additive and is composed of the separate atomic specific heats. (V. Kurbatov, 1914).

Table 2. Molecular Thermal Capacity of Aliphatic Halogen Derivatives

If we compare the temperature relations of molecular heats in Table 2 we see that:

- (1) The molecular heats of the simplest aliphatic halogen derivatives fluctuate within comparatively narrow limits from one to the other;
- (2) Increase of the weight of the halogens increases the molecular heat at 0 degrees, but not very substantially (by 1 - 2 units);
- (3) An increase in the number of halogen atoms increases the molecular heat at 0 degrees.

Table 3. Values for the Reduced Temperature Coefficients of Specific Heat

The reduced temperature coefficients, that is, the ratio $\frac{a}{b}$ of the constants in the formula $C_p = a + bt$, are compared in Table 3. While in the monohalomethanes (methyl halides) the value is comparatively small and equals 0.0017, in the case of monohaloethanes (ethyl halides) and the higher haloalkanes (alkyl halides) it is found to vary within the comparatively narrow limits: $\bar{M} = 0.0021 \pm 0.0003$.

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Thus, there seems to be a marked distinction between the methane bromide and iodide derivatives with a relatively small $E = 0.0016$ and the halogen derivatives of ethane and the higher alkanes, for which E approaches a value for alkanes. In further articles it will be shown that an increase in ionic bonds (as opposed to polar or covalent bonds) leads to a lowered reduced temperature coefficient of specific heat. From this it follows that an increase in ionic bonds takes place: (1) during transfer to hydrocarbons with a less extended chain (therefore the most pronounced ionic character must be ascribed to methane) or of the isomeric higher hydrocarbons, those which have the most uniformly branched chain (in the case of octanes) $(CH_3CH_2)_3C \cdot CH_3$; and (2) contain a greater number of heavier halogens are more strongly ionic.

Thus, the law that the reduced temperature coefficient of specific heat in organic compounds is equal to 0.0020 ± 0.0002 must be regarded as applicable in the case of halogen derivatives, beginning with the derivatives of ethane. The introduction of heavier halogens or a larger number of them increases the ionic bonds of the compounds and lowers the reduced temperature coefficient of specific heat.

Conclusions

1. The specific heat of 34 halogen derivatives (from methanes to pentanes) has been studied, at least under three temperature intervals.
2. It has been established that the temperature relationship is linear.
3. The introduction of chlorine increases the molecular heats at 0 degrees by 5.5. For Br the increase is 7; for I, 10; and F, 4.5.
4. The reduced temperature coefficient of the ethane halogen derivatives and higher homologs has a value of 0.0021 ± 0.0002 which is normal for organic substances.
5. The introduction of a greater number of halogens and the transfer of derivatives of methane lower the reduced temperature coefficient to specific heat to 0.0015.

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